BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(10), 2473—2475 (1974)

The Reaction of α-Olefins and Epoxyalkanes with the Dimethyl Sulfide–Sulfur Trioxide Complex

Masuzo Nagayama, Osamu Okumura, Katsumi Yaguchi, and Akira Mori
Central Research Laboratories, Lion Fat & Oil Co., Ltd., Hirai, Edogawa-ku, Tokyo 132

(Received March 2, 1974)

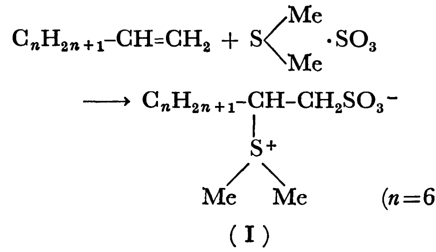
2-Dimethylsulfonioalkane-1-sulfonates were formed by the reaction of α-olefins with the dimethyl sulfide-sulfur trioxide complex. The treatment of these products with alkali gave Δ^1-alkene-1-sulfonates quantitatively. In the reaction between 1,2-epoxyalkanes and the dimethyl sulfide-sulfur trioxide complex, 1-dimethylsulfoniomethyl-1-alkyl sulfate was formed exclusively. 1-Dimethylsulfonio-1-alkenes were quantitatively formed upon the treatment of these products with alkali. The chemical structures of these compounds have been established, and the reaction routes were discussed.

The reaction product from an α-olefin with sulfur trioxide *i.e.*, an α-olefin sulfonate, is considered to be the base material of a new anionic surface-active agent, and a mechanism for the reaction has been proposed.[1,2]

Furthermore, numerous reports have been published on the chemistry of sulfonation using sulfur trioxide-Lewis base complexes.[3,4] We have now obtained some interesting results when the dimethyl sulfide-sulfur trioxide complex was used as the sulfonating agent in the sulfonation of α-olefins and epoxyalkanes; we will report those results in this paper.

Results and Discussion

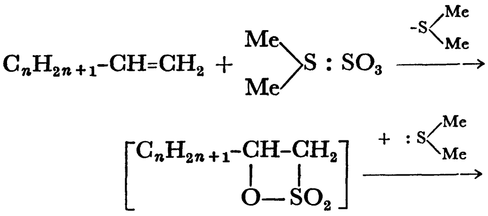
Reaction of α-Olefins with the Dimethyl Sulfide–Sulfur Trioxide Complex. Many studies have been carried out on the reaction between olefins and the sulfur trioxide-dioxane complex, particularly by Bordwell *et al.*[5–7] They considered that the zwitter ion was the initial sulfonation intermediate of this reaction; however, the zwitter ion has not actually been isolated. On the other hand we have ourselves proposed a new reaction mechanism in a previous paper.[4] An α-olefin was reacted with the sulfur trioxide-dimethyl sulfide complex, in ethylene dichloride at room temperature, to give a 2-dimethyl-sulfonioalkane-1-sulfonate (I) in a high yield. The structure of the product was established by IR and NMR spectroscopy.



$$C_nH_{2n+1}\text{-}CH{=}CH_2 + S(Me)_2\cdot SO_3 \longrightarrow C_nH_{2n+1}\text{-}\underset{\underset{Me\ \ Me}{S^+}}{CH}\text{-}CH_2SO_3^- \qquad (n=6, 8, 10, 12)$$

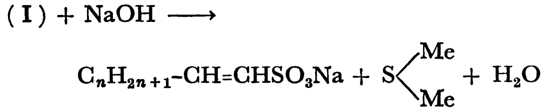
(I)

Sulfonium sulfonate internal salts have been synthesized either by the alkylation of mercaptoalkane sulfonates or by the addition of alkyl sulfides to sultones.[8] In the previous report, we established that the initial product of the reaction of α-olefin with sulfur trioxide is a β-sultone,[4] which immediately undergoes ring-opening by means of a nucleophilic reagent. It appears likely that the β-sultone is first formed in the present reaction also, and that it then reacts with dimethyl sulfide.



$$C_nH_{2n+1}\text{-}CH{=}CH_2 + \overset{Me}{\underset{Me}{>}}S : SO_3 \xrightarrow{-S(Me)_2} \left[\begin{array}{c} C_nH_{2n+1}\text{-}CH\text{-}CH_2 \\ |\quad\ \ | \\ O\text{—}SO_2 \end{array}\right] \xrightarrow{+\ :S(Me)_2} (\text{I})$$

In fact, we confirmed that the reaction between C_{12}-β-sultone, prepared by the previous method,[1] and dimethyl sulfide proceeds more rapidly than the reaction between the olefin itself and dimethyl sulfide. Also, in the former case the same 2-dimethylsulfoniododecane sulfonate internal salt was obtained in an excellent yield. Consequently, it may be considered that the formation of β-sultone is the rate-determining step. These internal salts decomposed easily with alkali to form Δ^1-alkene-1-sulfonates quantitatively.



$$(\text{I}) + \text{NaOH} \longrightarrow C_nH_{2n+1}\text{-}CH{=}CHSO_3Na + S\overset{Me}{\underset{Me}{<}} + H_2O$$

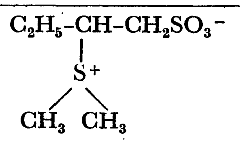
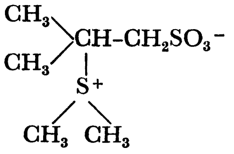
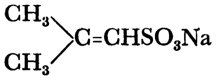
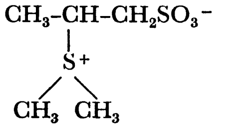
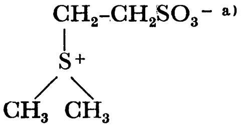
It is apparent that the α-hydrogen has become highly activated by both dimethylsulfonium and sulfonyloxy groups. The decomposed product was identified by means of the NMR spectra.

The decomposition rate was measured using a pH stat. It was dependent on the pH above 6, and consequently, this amphoteric surface active agent is unsuitable for use on the alkaline side. It was confirmed by NMR spectroscopy that the Δ^1-octene-1-sulfonate in the product obtained from 1-octene was a mixture of 61% *trans*-form and 39% *cis*-form, and this finding suggests that the alkaline decomposition proceeds by means of competitive E_2 and E_{1cb} processes.

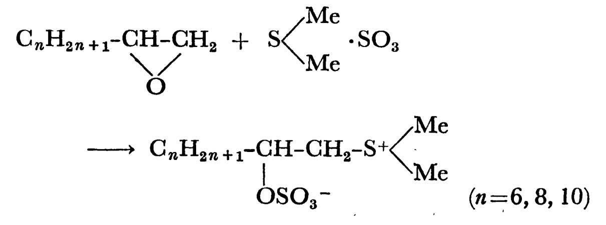
From olefins of a shorter chain length, similar sulfonation and alkaline decomposition products were obtained, as is shown in Table 1. From this table, a rather clear correlation between the yields and the electron-donating power of the alkyl groups of the olefins can be observed.

Reaction of Epoxyalkanes with the Dimethyl Sulfide-Sulfur Trioxide Complex. An epoxyalkane reacted with the dimethyl sulfide-sulfur trioxide complex in ethylene dichloride to give a 1-dimethylsulfoniomethyl-1-alkyl sulfate(II) quantitatively. The structure of the product was established by IR and NMR spectroscopy.

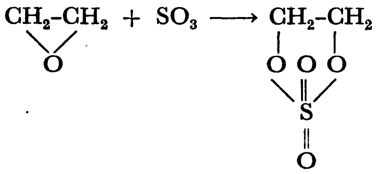
TABLE 1. REACTION PRODUCTS OF LOWER OLEFINS WITH DIMETHYL SULFIDE-SULFUR TRIOXIDE COMPLEX

Olefin	Product	Yield %	Found % C	Found % H	Calcd % C	Calcd % H	Alkaline decomposed product
1-Butene	 $C_2H_5\text{-}CH(S^+(CH_3)_2)\text{-}CH_2SO_3^-$	48	36.35	7.19	36.34	7.12	$C_2H_5\text{-}CH{=}CHSO_3Na$
Isobutene	 $(CH_3)_2C(S^+(CH_3)_2)\text{-}CH_2SO_3^-$	67	36.31	7.25	36.34	7.12	 $(CH_3)_2C{=}CHSO_3Na$
Propylene	 $CH_3\text{-}CH(S^+(CH_3)_2)\text{-}CH_2SO_3^-$	76	32.76	6.74	32.59	6.56	$CH_3\text{-}CH{=}CHSO_3Na$
Ethylene	 $CH_2(S^+(CH_3)_2)\text{-}CH_2SO_3^-$ [a]	trace	—	—	28.22	5.92	$CH_2{=}CHSO_3Na$

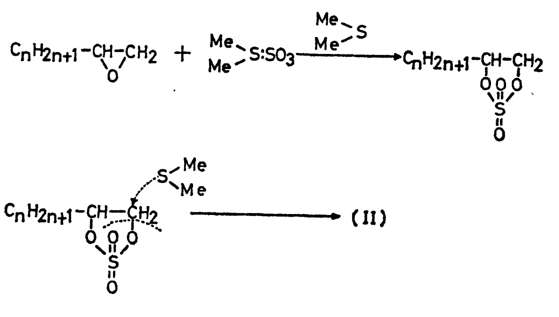
a) This product was not isolated, but identified by NMR spectrum, in reaction solution.


$$C_nH_{2n+1}\text{-}\underset{O}{CH\text{-}CH_2} + S(Me)_2\cdot SO_3 \longrightarrow C_nH_{2n+1}\text{-}\underset{OSO_3^-}{CH}\text{-}CH_2\text{-}S^+(Me)_2 \quad (n=6,8,10)$$
(II)

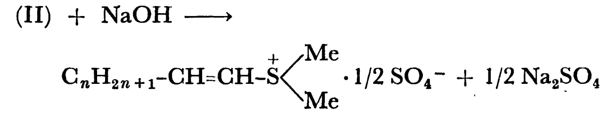
G. E. Ham has reported that SO_3 is inserted into ethylene oxide to form ethylene sulfate.[9]



Therefore, the mechanism of this reaction may be considered to involve the initial formation of alkyl-substituted ethylene sulfate, followed by ring-opening by means of S_N2 process with dimethyl sulfide.



The 1-dimethylsulfoniomethyl-1-alkyl sulfate (II) can be easily decomposed in an alkaline medium to form Δ^1-alkenesulfonium salt quantitatively.


$$\text{(II)} + NaOH \longrightarrow C_nH_{2n+1}\text{-}CH{=}CH\text{-}\overset{+}{S}(Me)_2\cdot 1/2\, SO_4^- + 1/2\, Na_2SO_4$$

In this case, it was also confirmed by NMR spectroscopy that the decomposed product was a mixture of 70% *trans*-form and 30% *cis*-form for $n=6$. The decomposition rate was measured similarly with a pH stat. It was dependent upon the pH. For example, the decomposition rate constant (at pH=9.0) is 0.0599 min^{-1}, about 80 times larger than that of the sulfonium-sulfonate (I) type mentioned above.

Ethylene oxide reacted similarly with the dimethyl sulfide-sulfur trioxide complex quantitatively.

As well as with dimethyl sulfide, the reaction also proceeded with methyl ethyl sulfide and diethyl sulfide. However, the expected products were not obtained with ethyl hexyl sulfide, suggesting that a steric effect may be an important factor in this reaction.

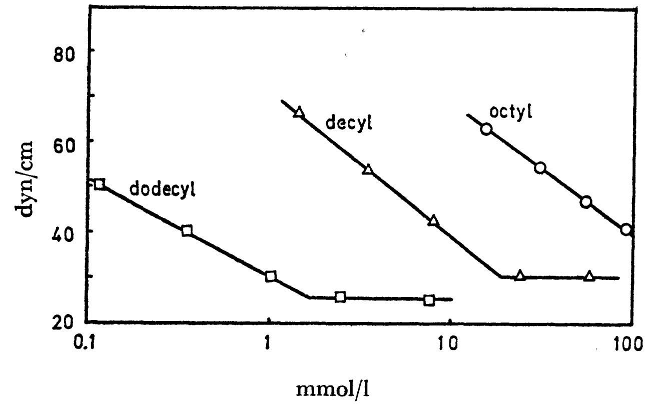


Fig. 1. Surface tension *versus* concentration of 1-dimethylsulfoniomethyl 1-alkyl (octyl, dodecyl) sulfate at 70 °C.

Surface-active Properties. 2-Dimethylsulfonioalkane-1-sulfonates have superior surface-active properties; Compound (I) with $n=8$ has an optimum surface activity, and its critical micelle concentration is 28 mmol/l and $\gamma_{\mathrm{cmc}}=30$ dyn/cm. Its wetting power is 11 s at 25 °C, 40 mmol/l and its forming height is 170 mm at 25 °C, 40 mmol/l.

1-Dimethylsulfoniomethyl-1-alkyl sulfates (II) also show good surface activities. The correlation between their concentrations and surface tensions is shown in Fig. 1.

Experimental

Materials. The sulfur trioxide (liquid and stabilized, manufactured by the Nisso Kinzoku Co.) was used after distillation. The C_{10}–C_{16} olefins (manufactured by the Gulf Oil Co.) were purified by distillation. The C_8—C_{14} epoxyalkanes were prepared according to the method of Swern.[10] The ethylene, propylene, 1-butene, and isobutene (manufactured by the Wako Junyaku Co.) were used as received.

Reaction of α-Olefins with the Dimethyl Sulfide-Sulfur Trioxide Complex. The case of 1-dodecene will be described as a typical example. Dimethyl sulfide (0.6 M) was dissolved in 100 g of ethylene dichloride, and the mixture was cooled to −10 °C. When 0.5 M of sulfur trioxide, dissolved in 50 g of ethylene dichloride, was stirred, drop by drop, into the dimethyl sulfide solution, a white precipitate of dimethyl sulfide-sulfur trioxide complex was formed, with the evolution of heat. When 0.6 M of 1-dodecene was added to the reaction mixture, the reaction solution became transparent. A white precipitate was gradually formed while the reaction temperature was maintained at 55 °C for 3 hr. The product was cooled to 0 °C, filtered, and then recrystallized from ethanol. The yield was 52% on the basis of the sulfur trioxide. Found: C, 53.79; H, 9.60; S, 20.4%; Calcd for $C_{14}H_{30}S_2O_3$: C, 54.15; H, 9.74; S, 20.7%. IR (KBr-disk); 1200 ($\nu_{S=O}$) cm^{-1}, 1045 ($\nu_{S=O}$) cm^{-1}. NMR; 7.05 (s, 6H, $\genfrac{}{}{0pt}{}{CH_3}{CH_3}\rangle\overset{+}{S}-$), 6.63 (d, 2H, $-CH_2SO_3^-$), 6.20 (m, 1H, $\rangle CH-\overset{+}{S}\langle$).

Reaction of the C_{12} β-Sultone with Dimethyl Sulfide–Sulfur Trioxide Complex. C_{12} β-sultone (0.1 M), prepared by the previous method,[1] was dissolved in ethylene dichloride (100 g). To this solution, dimethyl sulfide (0.11 M) was added at 0 °C, and the mixture was stirred for 2 hr, a white precipitate was gradually formed, filtered and then recrystallized from ethanol. 26.4 g (85% yield) of 2-dimethylsulfoniododecane-1-sulfonate were thus obtained.

Reaction of the Epoxyalkanes with Dimethyl Sulfide-Sulfur Trioxide Complex. The following procedure for the reaction with 1,2-epoxydodecane is typical. The dimethyl sulfide-sulfur trioxide complex was prepared by the method described above. To one equivalent of this complex, we added equivalents of 1,2-epoxydodecane. A white precipitate was formed when the reaction product was aged at 45 °C for 25 hr. The reaction product was filtered and recrystallized from ethanol. The yield was 85% on the basis of the sulfur trioxide. Found: C, 51.74; H, 9.26; S, 19.7%: Calcd for $C_{14}H_{30}S_2O_4$: C, 51.50; H, 9.26; S, 19.6%. IR (KBr-disk); 1300, 1250, 1100 ($\nu_{S=O}$) cm^{-1}. NMR; 5.30 (m, 1H, $CH-OSO_3^-$), 7.02 $\left(s, 6H, -\overset{+}{S}\langle\genfrac{}{}{0pt}{}{CH_3}{CH_3}\right)$, 6.33 (d, 2H, $-CH_2\overset{+}{S}\langle$).

Ethylene oxide was treated similarly to give 1-dimethylsulfonio ethane-2-sulfate in a 96% yield.

Measurements of Sulface-active Properties. The surface-active properties were measured by the JIS K-3362 method.

Measurements of the Decomposition Rates. The decomposition rate was measured at a given pH value in a pH stat(manufactured by the Toa Electronic Co., Model HS-1B). The amount of decomposed substances were calculated from those of the sodium hydroxide required to counterbalance the decrease in the pH with the progress of the reaction. The initial concentration of the substrate was 0.509 mmol/l; solvent, water; temperature, 48 °C; pH, 4.0—11.0.

References

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